

## Electronic structure and ionicity of actinide dioxides

P. J. Kelly (\*) M. S. S. Brooks and R. Allen

Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe 1, F.R.G.

**Résumé.** — Nous présentons des calculs de structure de bande par la méthode semi-relativiste LMTO pour les dioxydes d'actinide allant de  $\text{ThO}_2$  à  $\text{CmO}_2$  et pour différentes valeurs de l'ionicité des composés. Nous montrons que pour toutes les valeurs de l'ionicité, les niveaux 5f se déplacent de manière continue vers des énergies plus basses lorsqu'on augmente le numéro atomique. Pour une ionicité  $+2$  du cation et en utilisant l'approximation de la densité locale pour l'échange et la corrélation, nos résultats sont en bon accord avec ceux obtenus par photoémission et pour  $Z = 94$  (cas de  $\text{PuO}_2$ ) les niveaux 5f croisent la bande de valence.

**Abstract.** — We report semi-relativistic LMTO band structure calculations for the actinide dioxides from  $\text{ThO}_2$  to  $\text{CmO}_2$  for several values of the ionicity of the compound. It is found that for all values of ionicity the 5f levels move monotonically downwards in energy with increasing atomic number and that for an ionicity  $2+$  of the cation and using the local density approximation for exchange and correlation the 5f levels overlap the valence band at  $Z = 94$  ( $\text{PuO}_2$ ) in good agreement with photoemission experiments.

**1. Introduction.** — The actinide dioxides from  $\text{ThO}_2$  to  $\text{CmO}_2$  crystallize in the fluorite structure. We have calculated non self-consistent band structures and densities of states of the dioxides using Andersen's linear muffin tin orbital (LMTO) method [1] in the atomic sphere approximation (ASA) and have examined the effect of changing the ionicity and varying the exchange-correlation potential on the band structure and particularly on the sensitive 5f levels. Our results are compared with photoemission experiments.

**2. The model.** — We use the relativistic form of the LMTO method which has been shown by Freeman and Koelling [2] to be necessary for the actinides. This includes mass velocity and Darwin shifts but at this stage spin-orbit coupling has been omitted to make the calculation tractable. In the LMTO method we parameterize the logarithmic derivative  $D_l(E)$  at the sphere  $S$  as follows :

$$[D_l(E) - D_{v,l}]^{-1} \approx -[m_{v,l} \varepsilon]^{-1} + a_{v,l} + b_{v,l} \varepsilon$$

where  $\varepsilon \equiv (E - E_{v,l}) S^2$  and  $D_{v,l}$  is the value of the logarithmic derivative at the energy  $E_{v,l}$ . All the potential dependence enters the calculation through the parameters  $m_{v,l}$ ,  $a_{v,l}$ ,  $b_{v,l}$  and  $D_{v,l}$ . In particular the band mass  $2 m_{v,l}$  is an excellent measure of the width of the  $l$  band when  $E_{v,l}$  is the energy where  $D_{v,l} = -l - 1$  [1].

$\text{ThO}_2$  contains no f-electrons and the f-electron configuration of U in  $\text{UO}_2$  is probably  $5f^2$  (from

neutron diffraction experiments [3]). For the other dioxides we increase the actinide 5f level occupancy stepwise with increasing atomic number.

The ionicity of the dioxides is not definitely known and though it is often presumed [4] that U exists as  $\text{U}^{4+}$  in  $\text{UO}_2$  this is disputed by other investigators [5]. We have considered the cases of neutral,  $2+$  and  $4+$  actinide ions. In making the atomic calculations the problem arose of forming bound states for  $\text{O}^-$  and  $\text{O}^{2-}$ . This has been solved by putting a sphere of charge of opposite sign around the free ions to simulate the crystal background. The empirical Wigner-Seitz rules [6] were used to obtain a preliminary picture of the band positions and widths. These rules neglect all hybridization and though they do not give bandwidths very accurately they are useful for examining trends along the actinide series.

For the case of  $\text{UO}_2$  we examined several exchange-correlation potentials: the Slater  $X\alpha$  potential [7] (with  $\alpha = 1.0$ ), the Kohn-Sham potential [8] ( $\alpha = 2/3$ ) and a local density (LD) approximation [9]. It was found that the LD and  $\alpha = 2/3$  calculations gave very similar results while  $\alpha = 1.0$  produced 5f levels too low in energy. The energy bandwidths and placings as given by the empirical Wigner-Seitz rules for  $\text{UO}_2$  (ionicity =  $2+$ ) are shown in figure 1 for the three different exchange correlation potentials. We have found that the band structure is sensitive to the exchange potential mainly through the 5f levels as is the case for the actinide metals [2]. We therefore used the LD exchange correlation potential for all further calculations thus removing the arbitrary  $X\alpha$  parameter.

(\*) Department of Physics, The Polytechnic, Portsmouth, PO12DZ, England.

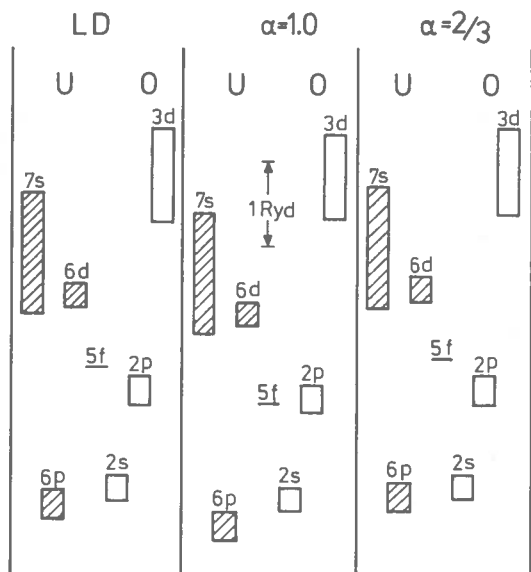


Fig. 1. — Effect of different exchange-correlation potentials on band placings and bandwidths of  $\text{UO}_2$  (ionicity =  $2+$ ) as given by the empirical Wigner-Seitz rules.

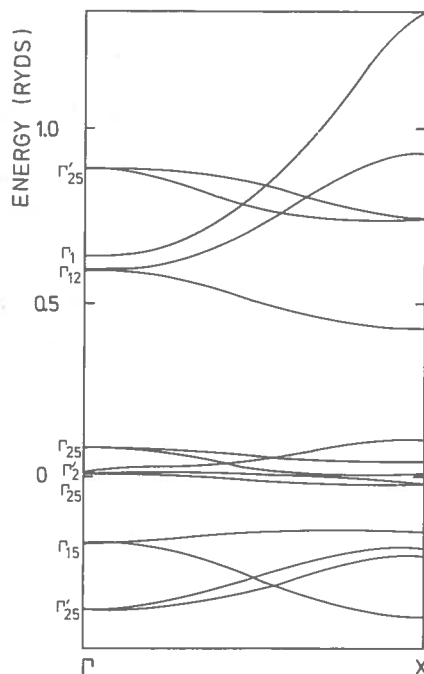
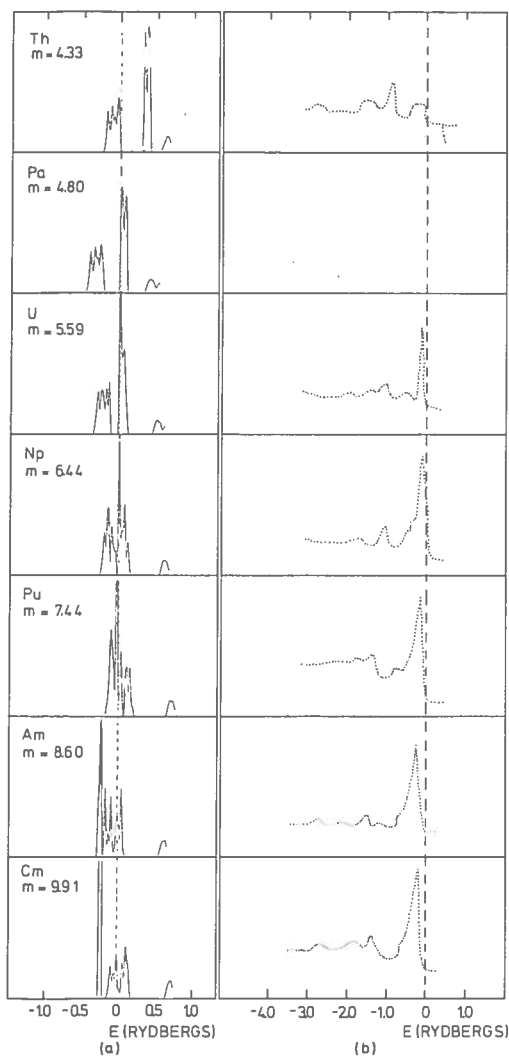


Fig. 3. — Band structure for  $\text{UO}_2$  (ionicity =  $2+$ , LD approximation to exchange correlation) along  $\Gamma X$  direction showing valence and conduction bands.



### 3. Results. — Our results show the following trends in the actinide dioxide series :

1) For all values of the ionicity the actinide 5f levels decrease in energy and narrow with increasing atomic number due to actinide contraction. Where they do not overlap the conduction or valence bands they have a width of between 1.9 and 1.5 eV which decreases with increasing atomic number.

2) With increasing ionicity the 5f levels always decrease in energy. For ionicity zero they lie too high and do not overlap the valence band even for  $\text{CmO}_2$ . For ionicity  $4+$  they lie too low being in the middle of the valence band for  $\text{UO}_2$ .

In figure 2 we compare the calculated densities of states for ionicity  $2+$  with the photoemission results of Veal, Lam, Diamond and Hoekstra [10] and find them in good qualitative agreement, with the 5f levels descending and overlapping the valence band for  $Z = 94$  ( $\text{PuO}_2$ ).

We find that the potential parameters  $a_{v,1}$  and  $b_{v,1}$  change by at most a few percent with increasing atomic number. However the band mass  $2m_{v,1}$  which

Fig. 2. — Comparison of density of states calculation for ionicity  $2+$  (a) with XPS spectra for actinide dioxides by Veal *et al.* (b). The states on the right in (a) form the bottom of the conduction band. In both (a) and (b) the 5f levels move down towards the valence band and cross into it for  $\text{PuO}_2$ . Note that the energy scales are not the same. The zero of energy is that of the highest occupied level and  $2m$  is the band mass for the 5f levels of the cation.

changes by at most 50 % from Th to Cm for  $l = 0, 1$  and 2 is found to change much more dramatically for the 5f electrons as shown in figure 2.

In figure 3 the valence and conduction bands of  $\text{UO}_2$  for ionicity 2+ in the  $\Gamma X$  direction are shown. Transitions from the  $\Gamma_{25}'$  bonding valence band to the low lying conduction bands ( $\Gamma_1, \Gamma_{12}$ ) are parity forbidden and  $\Gamma_{15} \rightarrow \Gamma_{12}$  transitions at the  $\Gamma$ -point produce the absorption edge. We note that the conduction band minimum and valence band maximum are not at the  $\Gamma$ -point.

**4. Conclusion.** — The results of our analysis show the effects of changing the ionicity and exchange-correlation potential on the band structure and give

the placing of the 5f levels in reasonable agreement with X-ray photoemission for ionicity equal to 2+ and using the LD approximation for exchange-correlation. We note that self-consistent molecular cluster calculations by Gubanov *et al.* [11] also give a uranium net charge of about 2+. It is less clear that the energy band gap is correct and experimental evidence is conflicting. Our view at present is that our gap is a little too large along the entire actinide series. The importance of fully self-consistent calculations, especially in ionic compounds with large transfer, cannot be overestimated and will hopefully supersede the modelled calculations described here.

It is a pleasure to acknowledge many useful discussions with Professor O. K. Andersen concerning the LMTO method.

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